

Chromium and Cadmium Replacement Options for Advanced Aircraft

Keith Legg

HCAT Program Review, KSC, Nov 2003



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Report Documentation Page

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Chrome replacement





Summary of best options

Technology	Applications	Limitations
Thermal spray (HVOF)	Landing gear, hydraulics, flap tracks	>0.001" thick Not IDs
Electroless Ni (Ni-P, Ni-B)	IDs, other NLOS, TDC alt.	Adhesion, build- up, heat treat
Nano Co-P electroplate	IDs, TDC alt., carrier LG?	Heat treat
PVD	Gun barrel IDs, small components	Cost <0.001" thickness
Plasma spray	IDs>3" (> 1.5" with new gun)	ID>1.5" >0.001" thick





Niche options

- Ion (Plasma) Nitride
 - > 500°C vacuum heat treat
 - Add oxide for corrosion resistance
- Electrocomposites
 - Electroplated Ni or Co with hard particles
- Laser cladding
 - Weld surfacing (also laser glazing, LISI, etc.)
- Electrospark deposition (alloying)
 - Localized repair and build-up
- Explosive cladding
 - Wide area bonding IDs, gun tubes, etc.





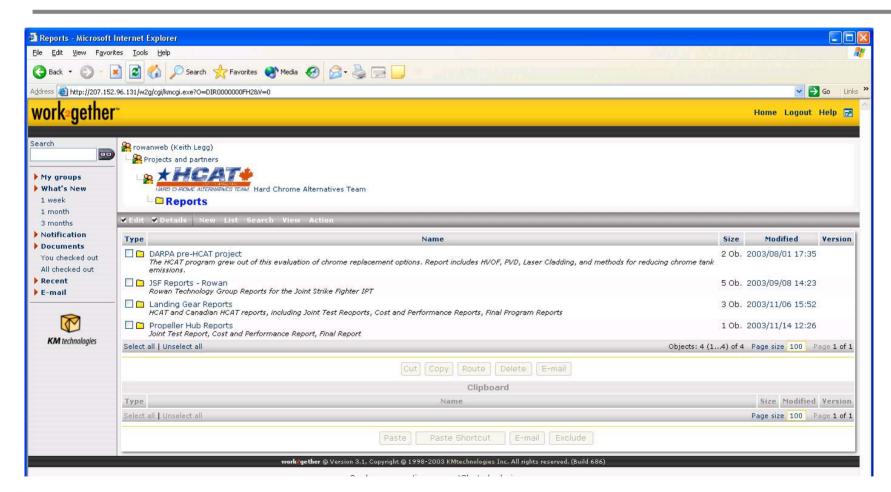
Data available

Large quantity of detailed performance data available from HCAT, including rig and flight tests; also commercial flight experience





HVOF – available data





Reports available

HCAT

- Landing Gear
 - Joint Test Report
 - Cost and Performance Report
 - Final Report (NRL report)
- Propeller Hubs
 - Joint Test Report
 - Cost and Performance Report
 - Final Report (NRL report)
- JSF Reports
 - HVOF as a Cr replacement
 - ID Cr alternatives
 - Repair options for Cr and Cd
- Original DARPA Cr options report

C-HCAT (Landing Gear folder)

- Heroux Devtek
 - Fluid compatibility
 - Grinding
 - > NDI
 - Stripping
- DND
 - Coupon testing
- Messier-Dowty
 - F-18 landing gear and drag brace rig tests (available shortly)
- Goodrich (available later)
 - Dash-8 rig test
 - Bend tests

Note: C-HCAT is all WC-CoCr



Applications - military

Qualified

- Landing gear components approved for HVOF coating at Hill AFB
 - A-10 MLG Piston
 - A-10 NLG Piston
 - B-1 MLG Axle
 - C-130 MLG Piston
 - C-141 MLG Bogie Beam
 - C-141 Outer Cylinder
 - C-5 MLG Roll Pin
 - C-5 MLG Ball Screw
 - C-5 MLG Outer Pitch
 - F-15 Drive Keys
 - KC-135 MLG Axles
- Messier-Dowty
 - CF-18 steering covers, piston heads, MLG hexagon repair
- F-22 (Raptor)
 - > F-119 engine, convergent nozzle actuators

Rig and flight test

- NADEP-CP, H-S, WR-ALC
 - EA-6B landing gear (flight)
 - P-3 bomb bay door actuators (flight)
 - E-2C, C-2, P-3, and C-130: prop tailshaft, low pitch stop lever sleeve, rocker land (rig)
- Lockheed
 - P-3 landing gear (rig)
- Messier-Dowty
 - > F-18 landing gear (rig)
- TF-33 engine, (P&W)
 - Accelerated Mission Test (AMT)
- NAVAIR PAX, Greene Tweed
 - Hydraulic actuator rig tests

F-35 – Goodrich
WC-CoCr baselined for piston and axle journals



Applications - commercial





Advantages and limitations

Advantages

- Much better wear resistance
- Lower seal wear (with proper superfinish)
- Takes a good finish (superfinish)
- Little or no fatigue debit
- Dry process, no embrittlement
- Easily stripped
- Widely available

Limitations

- Spalls at high cyclic bending load (close to yield)
- Spalls with high point or line load
- Coating can corrode (different mechanism)
- Cannot coat IDs
- Substrate heating (must control process)
- Must be done in booth (noise and dust, robotic)



Developments needed

More ductile HVOF coating

- Primarily needed for MRO (thick coatings)
 - Existing material fine for OEM use
- Avoid spalling at high load
- Will almost certainly have worse wear (softer)
 - But still better than EHC
- Use only where high bending or contact stresses
- May be a layered coating with ductile build and brittle overlay
 - Increased wear rate on breakthrough
- Same grinding wheel for steel and HVOF
 - Is being done commercially
 - Hill AFB tests under way looks readily doable





Summary of HVOF implementation issues

Integrity at high stress

- Issue only for thick overhaul coatings on carrier-based aircraft
- Sensitive to cyclic contact stress
 - Not seen in rig tests but should be watched

Masking

- Can be very personnelintensive
- Cannot use tapes
- Hard masking needed have to build up mask inventory

Grinding

- Need Al₂O₃ wheel for metal but diamond wheel for HVOF carbides
- Machine resetting or different grinding ROWAN PROCEDURES (feeds, speeds, Linking Glothubricants) Markets

Corrosion

- EHC does not corrode substrate corrodes and undercuts coating
- HVOF matrix (Co) can corrode, causing roughening, leakage, but not undercutting
 - Slow increases in leakage rather than catastrophic flaking
 - Seen with one operator's actuators in Europe – probably due to specific fluids or de-icers used only there

Embrittlement relief

 Hydrogen appears to diffuse slower through HVOF – may need longer H bake after Nital etch



Electroless Ni

Electroless Ni, being a Ni material, is next against the wall and is on the JSF Restricted Materials List.

Consider as an intermediate coating – a lot better than chrome, but likely to need replacement itself pretty soon.





Applications

- Wide variety of industrial applications
- Aircraft
 - GTE components P&W uses Ni-B various parts
 - Compressor blades (erosion, corrosion)
 - Shaft rebuilding
 - Flap tracks
 - Bearing journals





Advantages and limitations

- Advantages
- No electrodes
- No edge build-up
- Thin or thick
- A variety of EN composites available
 - > SiC
 - Diamond
 - Teflon

- Limitations
- Adhesion always a concern
- Requires 300-400°C heat treat for max hardness
- Hydrogen evolved during deposition
 - Does not seem to cause embrittlement
- Bath must be dumped periodically



Data available

- Like EHC electroless Ni has been around for so long that little data is available
 - Especially need comparison to EHC
- Some data available from vendors
 - Concern over reliability, accuracy
- Beware most data will be for heat treated state, but most airframe usage will be as-deposited
 - Wear not as good, corrosion better

- Studies of a number of electroless and electroplated Ni coatings being done by AFRL
 - Work ongoing
 - Typical hardness 700 850 HV
 - Good barrier corrosion, but no protection if breached (as with Cr)
 - http://www.materialoptions.
 com/w2g/cgi/kmcgi.exe?O=
 DIR0000000H81&V=0
 - joseph.kolek@wpafb.af.mil



Implementation issues

- Reliable adhesion is biggest production issue cited by aerospace users
- Requirement for heat treating for maximum hardness means that for many applications must be used as-deposited
 - Significantly lower wear resistance
 - Data needed for as-deposited and heat treated state





Nanophase Co-P

New coating developed by Integran of Toronto, Canada

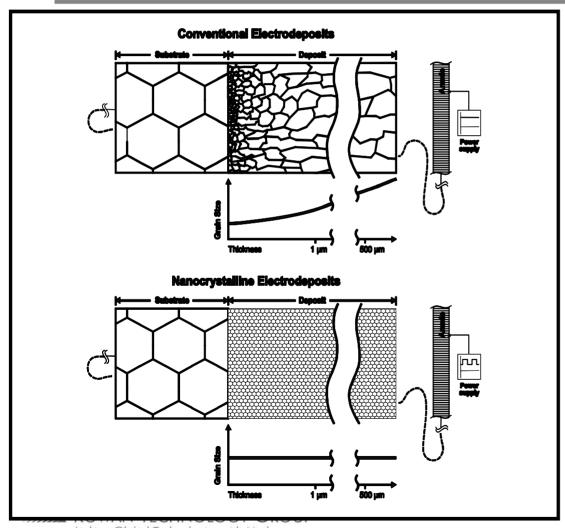
SERDP Project #1152, almost completed

http://www.materialoptions.com/w2g/cgi/kmcgi.exe? O=GRP000000H8F&V=0





Description



Pulse Plating favors
nucleation of new grains over
growth of existing grains,
resulting in an ultra-fine grain
structure throughout the
entire thickness of the
coating, right from the
substrate interface.

Typical deposition conditions

2ms pulses

125Hz, **25% duty cycle**

2 - 3V, 150mA/cm²



Advantages and limitations

Advantages

- Drop-in
 - Wherever EHC can go Co-P can go
- Better corrosion than EHC
- Little or no embrittlement
 - May work for field repair
- Looks usable to replace EHC, TDC, brush Cr

Limitations

- ESOH
 - OSHA pel for Co (8hr TWA) = 0.1 mg(Co)/m³
 - OSHA pel for metallic Cr (8hr TWA) = 1 mg(Cr)/m³
 - Co not known carcinogen
 - No regs at this time
- Heat treat for best hardness
- Requires pulse power supplies
 - Capital cost





Data available

Info at

http://www.materialoptions.com/w2g/cgi/kmcgi.exe?O=GRP0000000H8F&V=0





nCo-P structure

Nano Co-P alloy coatings developed under SERDP project PP-1152 as an environmentally-benign replacement for hard Cr coatings for NLOS applications.

Synthesis of Nanocrystalline Co-P Alloys

- Electrodeposition parameters modified to yield deposits with average grain sizes below 100nm
- Pulsed Current Deposition
- Plating Efficiency >90%
- Deposition rate 2-8 mills/hr
- Consumable & nonconsumable anode

Coating Thickness and Integrity of Nano Co 2-3wt%P

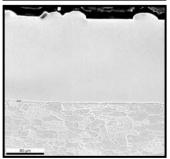
Surface Morphology

- Nodular, cauliflower morphology
- No pits, cracks, pores

Cross-Section

- Thickness ~135µm
- No pits, cracks, pores







Implementation issues

- ESTCP program approved between HCAT, Lockheed, Curtiss-Wright, Smiths Aero, NADEP JAX, OO-ALC to validate for ID EHC and for TDC replacement
 - Will begin January 04
 - Primary issues:
 - Ocan it work as a TDC alternative?
 - Heat treat requirements to meet TDC requirements
 - Embrittlement is it really non-embrittling?
 - Long term bath and process stability in depot environment (processing many different items)



Physical Vapor Deposition (PVD)

PVD involves deposition from a solid material source – evaporation, sputtering, arc





Applications

- Limited applications in aerospace
- Major application is TBCs
 - E-beam evaporated ZrO₂
- Wear resistance
 - > TiN
 - Bearing races and retainers
- Blade erosion
 - MDS Prad coating
- Fretting
 - > AlCu
- Low friction
 - Variations of MoS₂





Advantages and limitations

Advantages

- Very hard, wear resistant
- Reproducible, high quality
- Smooth
 - No finishing needed
- Probably good TDC alternative
- Many vendors
 - Esp. for TiN, DLC

Limitations

- Cost
- Thin (typically 3μm 0.0001")
 - Cannot be used for rebuild
- Lack of specs
- Vacuum requirements
 - Size limitations
 - Substrate temperature typically >250°C
 - Less reliable at low T
 - High cleanliness
 - Line of sight





Data available

- Large amounts of data available for many PVD coatings
 - Most in R&D journals
 - Little or no publicly available data for aerospace production use





Implementation issues

- Best applications for thin wear- or RCF-resistant items for max life (difficult to strip)
 - Items that will not be refurbished
 - Pins, gears, bearings
 - Niche applications
- Need data on wear and seal performance
- Easy to make components into cutting tools, esp with gears
- ID hard coatings under development
 - Marshall Labs, Paradigm Shift Techs



Plasma spray

Plasma spray guns can be small and the stand-off distance (gun-substrate) is much less than with HVOF





Applications

- Already specified for various repairs and build up in GTEs and airframes
 - Often used for same-material dimensional restoration
- In general new applications use HVOF rather than plasma spray
 - Plasma spray cheaper but quality lower
- Good method for coating IDs
 - Most guns only capable of coating >3" ID
 - New Sulzer Metco F-300 gun >1.6"
 - Makes most sense when already use HVOF for OD, so can do ID and OD with same spray booth, robot, etc.

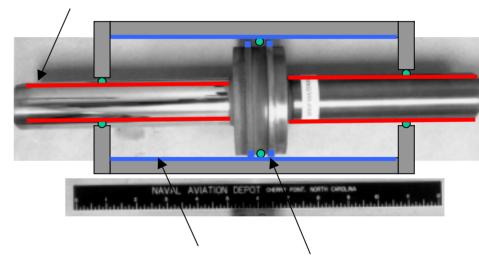




CH-53 helicopter blade damper

- Approved for repair
- T400 plasma spray on ID
- Typical actuator coatings:
 - Rod HVOF/D-gun WC-Co, WC-CoCr, WC-CrNi
 - Piston HVOF/D-gun WC-Co, T400
 - > ID plasma spray T400

HVOF/D-gun WC-Co (rod)



Plasma spray Tribaloy 400 (ID, piston)





Advantages and limitations

Advantages

- Similar to HVOF
- Able to coat inside IDs down to 3" ID for most guns, 1.6" for Sulzer F-300 gun

Limitations

- Adhesion not as good as HVOF
 - > 3-7 ksi vs >10 ksi
- Lower porosity than HVOF
 - > 10% vs 1 2%
 - Can allow leak-by in gas-over-fluid systems
- Requires grind, superfinish
 - More difficult for ID than OD



Data available

Nowhere near the amount of data available for HVOF. ID coating data available from HCAT ID plasma spray program.

http://www.materialoptions.com/w2g/cgi/kmcgi.exe? O=GRP000000GOW&V=0





Implementation issues

- May need to be sealed for some hydraulic applications
- Surface finish not well defined likely to need superfinish
- Design of air sweep to take heat and overspray from ID
- Plunge-grinding specs for OEM pistons
 - Coat piston, then plunge-grind seal groove



Conclusions on Cr replacement options

- HVOF is the method of choice for most ODs
 - WC-CoCr wherever possible for better corrosion resistance
 - > Where stress is too high we will need a more ductile coating
 - Maybe nCo-P, electro- or electroless Ni, or similar, trading wear life for coating integrity
- For IDs standard HVOF not viable
 - Electro- and electroless plating
 - Widest applications, including thin dense and flash Cr replacement
 - > ID plasma spray
 - Most cost-effective when using HVOF or other thermal spray for OD
 - > PVD

Linking Global Technologies with Markets

- Niche applications because of cost and complexity
- Could be broadened with reliable vendors, data, specs,
 especially for TDC replacement



Cadmium replacement options





Usage

Steel Components

- The "cure-all" corrosion coating
- Good salt spray and scribed corrosion protection
- No hydrogen embrittlement or stress corrosion cracking
- ODs and IDs
- Plate steel to protectAl



Fasteners

- Correct lubricity

 (avoid changes to torque-tension specs)
- No hydrogen embrittlement
- Retain thread profile

Connectors

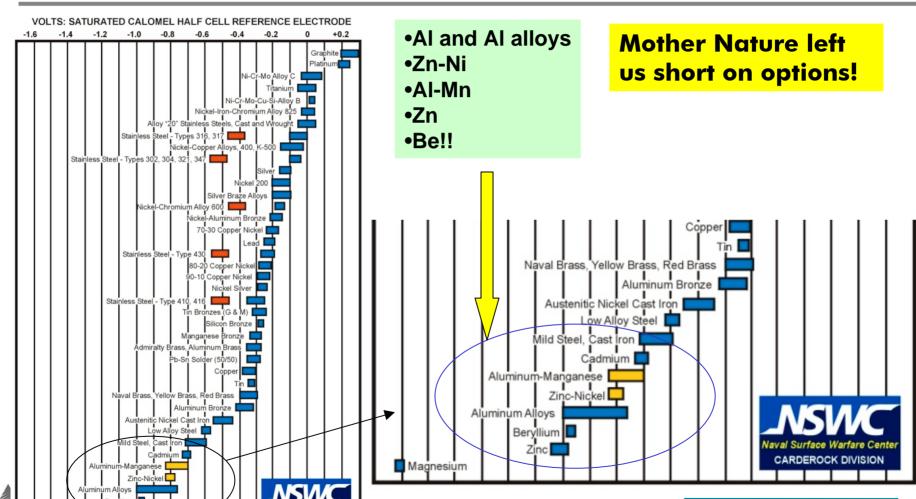
- For electrical equipment
- Low contact resistance
- Non-insulating corrosion products
- Solderable a plus





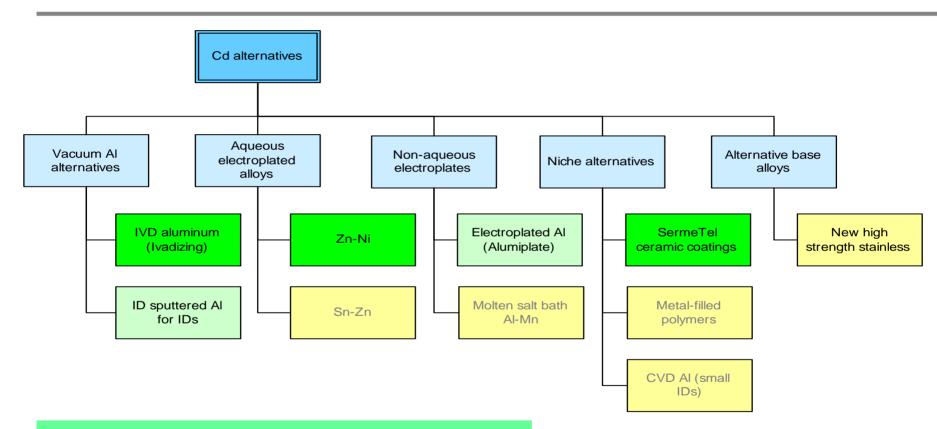


Galvanic series





Summary of Cd alternative options



All is the only "global" replacement Almost everything needs chromate conversion





JSF Cd Alternatives Report

- Requirements
- Alternatives
 - Zn-Ni, Sn-Zn electroplates
 - Alumiplate
 - Al-Mn molten salt bath
 - IVD and CVD Al
 - Sputtered Al
 - Thermal spray
 - SermeTels

Linking Global Technologies with Markets

- Filled polymers
- High strength stainless

http://www.materialoptions.com/w2
g/cgi/kmcgi.exe?O=DIR000000GK

WAQ TECHNOLOGY GROUP

LINKING GLOBAL TECHNOLOGIES WITH MARKETS



Joint Strike Fighter

Courts by Photographer's Mate 2nd Class Shene MinCoy

Report to: William Green Geo-Centers

Rowan Project #: 3105JSF3

Contract Number: N00173-98-D-2006, D.O. 0002 Subcontract Number: GC-3363-99-004 P.O. Number: 2857-8MK

Report Number: Final Date: December 18, 2000

Author: Keith Legg klegg@rowantechnology.com

This document is approved by Kathy Crawford for Distribution Statement A - Unlimited Distribution under JSF Case Number 35F01-0138 as of 23 Aug 01



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Joint Test Report

- Cd alternatives report for low strength steels (<220 ksi)
 - Boeing, JGPP
 - > Sn-Zn
 - Acid Zn-Ni (Boeing)
 - Alkaline Zn-Ni
 - > IVD AI

http://www.jgpp.com/projects/cadmium/
itr.html

http://www.materialoptions.com/w2g/cgi/kmcgi.exe?O=DIR00000016D&V=0



Engineering and Technical Services for Joint Group on Pollution Prevention (JG-PP) Projects

> Joint Test Report BD-R-1-1

for Validation of
Alternatives to Electrodeposited
Cadmium for Corrosion Protection and Threaded
Part Lubricity Applications

October 1, 2002

Distribution Statement "A" applies.

Approved for public release; distribution is unlimited.

Contract No. DAAE30-98-C-1050 Task No. N.272 CDRL A006

Prepared by: National Defense Center for Environmental Excellence (NDCEE)

> Submitted by: Concurrent Technologies Corporation (*CTC*) 100 *CTC* Drive Johnstown, PA 15904



IVD AI

Vacuum PVD process
Fully qualified and quite widely used by OEMs and depots
Spec MIL-C-83488 for Al coating does not define deposition method





Applications

Military

- > F-4
- > F-14
- > F-15
- ▶ F-16
- > F-18
- > AV-8B
- > A-12
- > V-22
- Apache

Commercial

- Boeing 737, 747, 757, 767
- McDonnell-Douglas DC9, 10, MD-80, 90, 11
- Bombardier Dash 7, 8
- Airbus A300, A310



Advantages and limitations

Advantages

- Qualified commercial process
 - Commercial coating shops
 - IVD-coated fasteners available commercially
- Clean and safe
- Good performance
- No H embrittlement

Limitations

- Vacuum process
 - **Expensive**
 - Awkward
- Poor quality coating asdeposited
 - Peen and chromate
- Poor throwing power
- Soft and easily damaged
 - Cannot easily be repaired
- Dissolves in alkaline cleaners
 - MRO users may have to change cleaning process





Data available

Data available from Boeing, JGPP report

http://www.jgpp.com/projects/cadmium/jtr.html

http://www.materialoptions.com/w2g/cgi/kmcgi

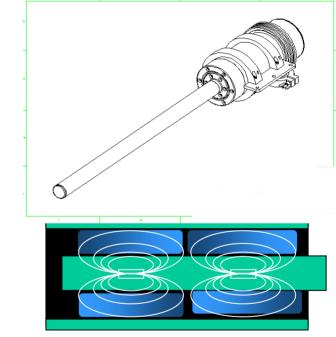
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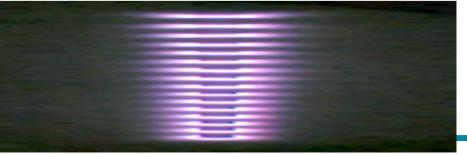




PVD Al for IDs – sputtered Al

- Marshall Labs Plug and Coat
 - Works inside IVD chamber
- Makes it possible to coat OD and ID simultaneously Plug
 Coat
 - Add-on to existing IVD chamber
- □ Status
 - Being installed at Hill AFB
 - Commercially available
 - Meets MIL Spec.
- Note: All Al coatings require use of proper aqueous cleaners (avoid alkaline cleaners)







Developments needed

- Some additional environmental embrittlement data needed
- Plug and Coat miniaturization needed for smaller IDs
 - Under way at Marshall Labs
- Porosity and need for peening always an issue
 - Various approaches for better coating quality
 - Higher plasma density
 - Sputtering instead of IVD
 - Pulse biasing





Electroplated Al (Alumiplate™)

Alumiplate, Minneapolis

Deposited from organic solution

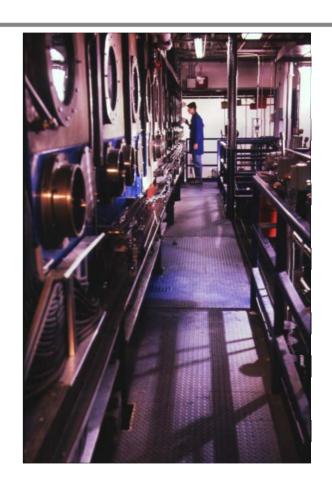




Alumiplate description

Organic electroplate

- Requires enclosed tank and plating line in inert environment
 - Similar to vacuum processing but less
- Al salts in toluene solution
- Reasonable throwing power
 - Needs conformal or secondary electrodes for complex shapes, IDs
- Frequently uses Ni strike for adhesion
- Recent development uses grit blasting and activation with no Ni strike
 - Equivalent adhesion
- Metallic strike needed for insulators such as composites
- Coating thickness 0.0001 0.001"
 - Usually 0.0003 0.0005"
- Conversion coat (traditionally chromate) for best corrosion performance (as with all other Cd alternative)





Advantages and limitations

Advantages

- "Drop-in" replacement
- Able to coat complex shapes
- Higher quality coating than as-deposited IVD AL
- Suitable for components, connectors, fasteners (with dry lube)
- Directly compatible with Al skins
- Can be anodized for better wear and abrasion

Limitations

- Size limited
 - Landing gear about 3' long
 - Limited by current bath size
 - > Appears scalable
- Requires dry lube for threads to prevent galling
- Sole source is Alumiplate, Minneapolis
 - Willing to license, but no current licensees
 - Not yet available in Europe
- High capital cost
- Toluene bath not suitable for DoD depot use
- Cannot brush plate Al repair
 - Can brush plate Sn-Zn to repair Al





Data available

A great deal of data becoming available as a result of ongoing JSF and Army testing. Rowan is currently putting together a report on the technology – available by year's end





Electrical connectors

- Meets all tests for qualification on connector shells (MIL-DTL-38999K testing)
 - Al and C-fiber/PEEK composite
 - Corrosion, conductivity stability in salt fog
 - Mate/unmate testing (wear, torque, conductivity)
 - No insulating corrosion products
- Amphenol has now assigned part numbers for commonly-used AlumiPlated aerospace connectors



Other issues

Repairability

- Al can be repaired by brush plating Sn-Zn after suitable activation (Boeing)
- Can also be repaired with brush-on SermaTel

Anodizing

- Can be anodized, leaving Al layer beneath anodize layer
- Will improve wear and abrasion, but hard coating on soft underlay not a good high load wear surface

Any form of Al avoids Cd embrittlement

- Very bad form of embrittlement
- Can occur when aborted takeoff heats brake discs and nearby landing gear components





Developments needed

- Non-toluene solution needed for depot use
 - Present chemistry cannot be used in depots
- Additional sources for plating service
- Additional embrittlement testing
- Well-defined brush plate or other repair
 - Both for OEM and MRO use





Other ways to deposit Al

Arc or flame spray

- Used on some Bombardier aircraft
- Thick coating (0.001 0.003")
- Rough
- Al-Zn arc spray used on support equipment, radar towers, bombs

CVD

- Generally high temperature
- Used for cooling passages in hot section blades
- AFRL SERDP project approved for FY 04
- Slurry Al developed by Liburdi Engineering
 - High temperature heat treat
 - For hot section turbine blades (oxidation resistance)





SermeTel®

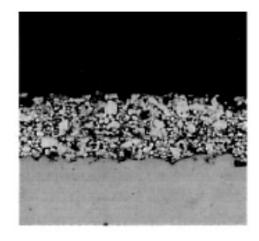
Metal-filled ceramics from SermaTech





SermeTel

- Al flakes in ceramic matrix
- Brush or spray on
- Older formulations contain Cr⁶⁺
- Heat treat 375-700°F
 - Hard, glassy coating
- Grit blast to uncover Al



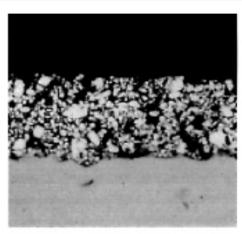


Figure 17. SermeTel aluminum-ceramic coating cross sections 500x. Left chromate-containing coating; right chromium-free coating.



Applications

- Used in turbine engines
 - Cases and discs
- Landing gear in some older aircraft (commercial)
- □ F-22
 - Extensive use of SermeTel coatings on landing gear and other systems
 - See Baltimore meeting on Materials Substitution for P2 in Advanced Aircraft (2002)



Advantages and limitations

Advantages

- Simple spray or paint
 - Can be used for repair
- Hard coating
 - Abrasion resistant

Note: There are now some other similar coatings on the market

Limitations

- Sole source
 - Licensing to major users only (e.g. Goodrich)
 - Others (inc. depots) must send to SermaTech
 - Very high cost
- Requires heat treat
 - Can be low enough T for HSS
- Embrittlement from acids in formulation
 - When using 984/985 HE on A100 for F-22
 - New formulation, not yet tested or approved
- Contains chromates
 - New non-chromate formulations now available





Data available

Little publicly available data





Zn-Ni electroplate





Applications

- Boeing uses acid Zn-Ni
 - Restricted to UTS<220 ksi because of embrittlement issues</p>
- Oklahoma City ALC
 - Replaced Cd and TiCd with brush Cd, Zn-Ni and IVD in 1991





Advantages and limitations

Advantages

- Aqueous electroplate
 - Easier application in open tanks
- Qualified process
- Tank and brush plate

Limitations

- Alloy chemistry
 - Difficult to ensure reproducibility and uniformity, especially on complex shapes
- Embrittlement



Data available

Data available from Boeing, JGPP report

http://www.jgpp.com/projects/cadmium/jtr.html

http://www.materialoptions.com/w2g/cgi/kmcgi

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Developments needed

- Extension to high strength steels
 - New JTP for HSS under way Boeing, JGPP
- Brush plating
 - Is Zn-Ni a good repair for IVD or electroplated Al?





High strength stainless steel

S-53 – new steel developed by QuesTek Innovations LLC





Advantages and limitations

Advantages

- No coating to come off
- Eliminates corrosion
 - Primary cause of landing gear overhaul and parts condemnation
- Avoids SCC
 - Primary mechanism for major landing gear failure

Limitations

- Cannot be used uncoated against Al
- More expensive than 300M
 - A bit less than cost of A100



Developments needed

- Full validation of properties and performance
- Development of materials database
- Licensing to steel producers so commercially available
 - QuesTek's intent is licensing to several steel companies (QuesTek is a steel developer, not a producer)





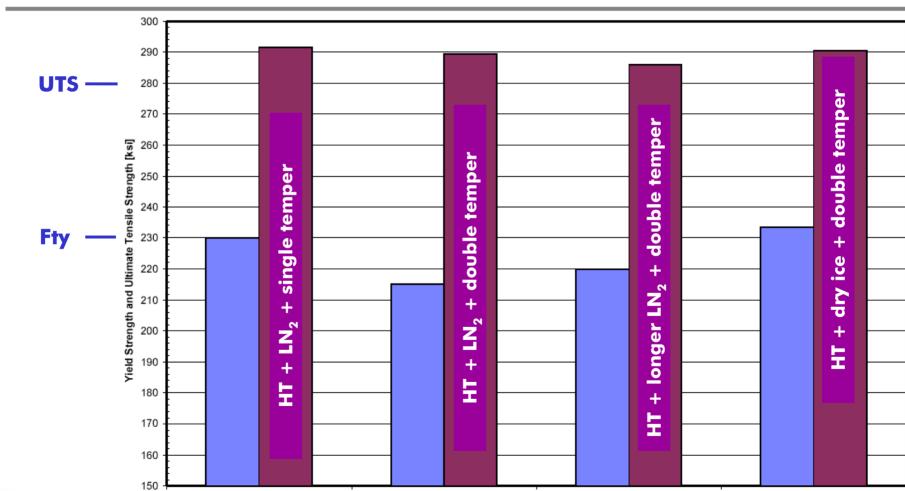
Data available

Extensive data will become available over next 2 years from ESTCP program





HSSS properties





Current status

- Appears to be mechanically equivalent to 300M but much better fracture strength and SCC
- Being tested and validated at Hill AFB
- Work to be complete in 3005
- Will obtain data needed for qualification
 - Not MIL Handbook 5 (requires 10 heats at \$300,000/heat)
 - Will do three heats to 20,000 lb
 - Then use AIM method (Accelerated Insertion of Materials) to interpolate between and extend lab data using modeling data



Conclusion on Cd alternatives

- Al is the best overall option, but deposition methods are not straight "drop-in"
 - Electroplated Al looking increasingly good for OEMs
 - If adopted broadly, what about depot repair?
 - Non-toluene electroplate? IVD + sputtering?
- High strength stainless exciting new development
 - Will be 2 or 3 years before it is fully qualified at Ogden
 - Even then, no MIL Handbook 5 numbers
 - Modeling will tell us more about this steel than we know about most others

